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DIRECT DETERMINATION OF DOUBLE BOND POSITION IN LONG CHAIN CONJUGATED DIENES BY t.$C_4H_9^+$ - CHEMICAL IONIZATION MASS SPECTROMETRY .

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ABSTRACT : t.$C_4H_9^+$ - chemical ionization mass spectrometry of long chain conjugated dienes was shown to generate branched alkyl cations providing unambiguous location of the unsaturated system .

Aliphatic alcohols, acetates or aldehydes containing conjugated diethylenic systems are common structures found in the insect pheromones . In several Lepidopteran species of economic importance[1], these compounds can play a major role in the sexual behaviour and consequently also in the synthetic formulations used for agricultural pest management . During their identification from pheromonal extracts, localization of the double bonds usually necessitates chemical derivatization[2] or oxydative degradation[3] prior to GC-MS analysis . Due to the low quantities of material available (10^{-2}-10 µg), we have investigated less consuming methods through gas phase ion-molecule reactions . This type of reaction which may lead to a specific fragmentation of unstable adduct-ions has been applied to locate various functional groups[4] . However, in the case of conjugated dienes, no specific data have been published so far . We report herein our findings about the reactivity of the t.$C_4H_9^+$ cation on these systems[5] .

Straight chain C_{10}-C_{18} conjugated dienes with/or without a primary oxygen function have been analyzed (Table 1) under t.$C_4H_9^+$ - CIMS conditions[6] . The mass spectra generally display the molecular species $M^{+\cdot}$ (charge exchange process), $[M + C_4H_9]^+$, MH^+ and subsequent $[MH-H_2O]^+$ (cf. diene-alcohols or aldehydes), $[MH - CH_2CO]^+$, $[MH - AcOH]^+$ (cf. diene-acetates) ions of relatively (except for the $[M + C_4H_9]^+$ adduct-ion) high abundance . Series of $[C_nH_{2n-1}]^+$ and $[C_nH_{2n-3}]^+$ ions can also be observed . Of more interest is the occurrence of one or two intense (except for diene-acetates) peaks (A^+ and B^+ ions) at m/z values depending on the position of the conjugated diene system along the chain (Figure 1 ; Table 1) . However, for terminal positions of the diene (Table 1, compounds 8 and 10), both ions A^+ and B^+ do not appear .

To determine the origin of these fragment ions, MS-MS studies were performed on various model molecules using a triple quadrupole instrument[7,8] . Constant daughter ion spectra did not permit to detect any significant precursor ion for A^+ and/or B^+ . On the other hand, constant

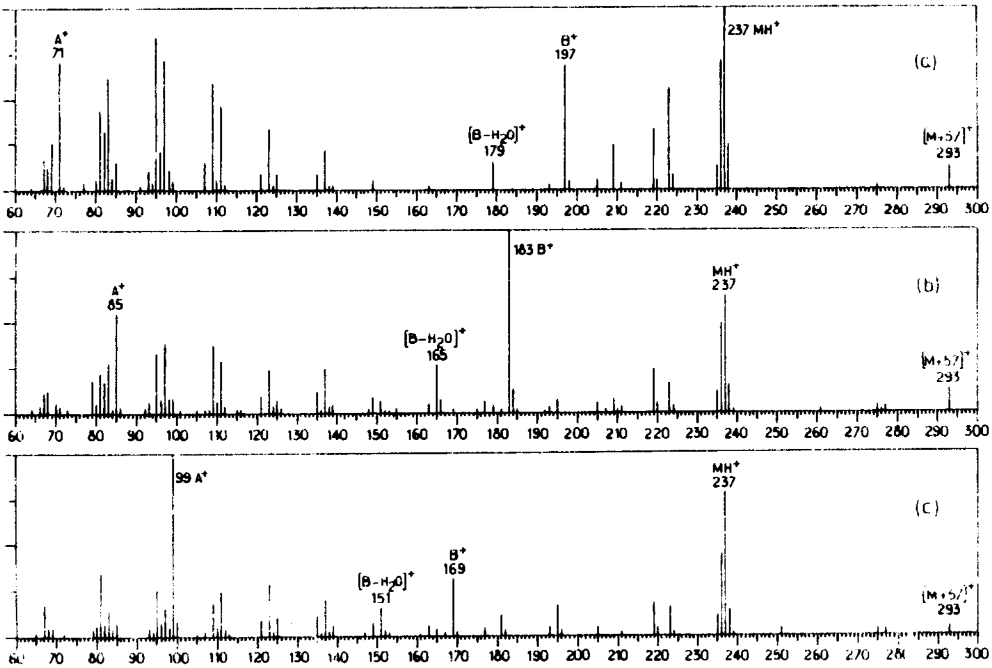
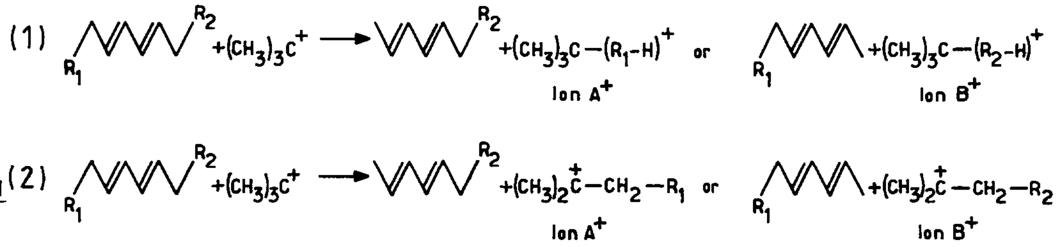


Figure 1 - t.$C_4H_9^+$ - CI mass spectra of (Z,Z)-11,13 hexadecadienal 21 (a), (Z,E)-10,12 hexadecadienal 22 (b) and (E,Z)-9,11 hexadecadienal 23 (c) .

parent ion spectra (or CAD spectra) of the molecular species $[M + C_4H_9]^+$, MH^+ and $M^{+\cdot}$ did not exhibit, in any case, ions A^+ and/or B^+ in significantly high abundance, which excludes the former ions as possible precursors in the free field region .

Both these results thus suggest that ions A^+ and B^+ are mainly generated in the source from an unstable $[M + C_4H_9]^+$ intermediate adduct-ion . As indicated by preliminary D-labelling studies, such an intermediate should decompose by allylic cleavage (Scheme 1) and simultaneous attachment of (formally) a C_4H_8 unit according to two pathways (the origin from either the diene or the $C_4H_9^+$ cation of the necessary H transfer has not yet been determined) . The structure of the branched alkyl ions (t-butyl or i-butyl group) thus obtained was demonstrated by studying CAD spectra of A^+ and/or B^+ from diene-aldehydes or alcohols . Indeed, the expected predominant $[A - C_4H_8]^+$ and $[B - (C_4H_8 + H_2O)]^+$ ions could be observed as main daughter ions of A^+ and B^+, respectively . The constant neutral mass spectra for loss of C_4H_8 (56 a.m.u.) or successive losses of C_4H_8 and H_2O (74 a.m.u.) showing A^+ and B^+, respectively as main



Scheme 1

Table 1 - Main diagnostic ions from $t.C_4H_9^+$ - CI mass spectra of conjugated diene-alcohols, acetates or aldehydes and conjugated alkadienes (intensities given relatively to the base peak) .

Compound	$[M+C_4H_9]^+$	MH^+	M^+	A^+	B^+	$[B-H_2O]^+$
1 (E,E)-11,13 hexadecadien-1-ol	295 (8)	239 (100)	238 (49)	71 (13)	199 (23)	181 (1)
2 (E,Z)-10,12 hexadecadien-1-ol	295 (5)	239 (100)	238 (42)	85 (36)	185 (11)	167 (1)
3 (E,E)-8,10 tetradecadien-1-ol	267 (2)	211 (100)	210 (50)	85 (37)	157 (34)	139 (3)
4 (E,E)-7,9 tetradecadien-1-ol	267 (4)	211 (100)	210 (55)	99 (39)	143 (29)	125 (18)
5 (E,E)-8,10 tridecadien-1-ol	253 (4)	197 (100)	196 (52)	71 (22)	157 (32)	139 (2)
6 (E,E)-7,9 tridecadien-1-ol	253 (4)	197 (100)	196 (72)	85 (20)	143 (38)	125 (8)
7 (E,Z)-8,10 dodecadien-1-ol	239 (8)	183 (73)	182 (25)		157 (20)	139 (3)
8 (E,E)-8,10 undecadien-1-ol	225 (10)	169 (59)	168 (21)			
9 (E,E)-6,8 undecadien-1-ol	225 (2)	169 (78)	168 (35)	71 (18)	129 (16)	111 (9)
10 (E,E)-2,4 decadien-1-ol		155 (3)	154 (10)			
11 (E,E)-11,13 hexadecadienyl acetate	337 (<1)	281 (100)	280 (42)	71 (7)	241 (6)	
12 (E,E)-9,11 tetradecadienyl acetate	309 (<1)	253 (90)	252 (37)	71 (11)	213 (6)	
13 (E,E)-7,9 tridecadienyl acetate	295 (1)	239 (78)	238 (29)	85 (1)	185 (2)	
14 (E,E)-8,10 dodecadienyl acetate	281 (2)	225 (60)	224 (18)		199 (1)	
15 (E,Z)-10,12 hexadecadienal	293 (2)	237 (100)	236 (49)	85 (100)	183 (29)	165 (9)
16 (E,E)-8,10 dodecadienal	237 (2)	181 (100)	180 (35)		155 (45)	137 (23)
17 (E,Z)-7,9 dodecadienal	237 (6)	181 (100)	180 (28)	71 (64)	141 (22)	123 (27)
18 (E,E)-2,4 hexadecadiene	279 (8)	223 (63)	222 (100)		197 (78)	
19 (Z,Z)-5,7 dodecadiene	223 (1)	167 (54)	166 (100)	99 (42)		
20 (Z,Z)-3,5 undecadiene	209 (1)	153 (51)	152 (74)	71 (31)	113 (36)	

parent ions (base peaks) for these specific eliminations confirmed this assumption . In addition, ions A^+ and B^+ were proved to be major precursors for an ion at m/z 57 (constant daughter ion spectra) .

Finally, the production through ion-molecule reaction of branched alkyl cations (A^+ and/ or B^+) from long chain conjugated dienes using $t.C_4H_9^+$ as reagent is highly specific (compared to monoenes[4c] or unconjugated dienes[9]). With a few exceptions, this method can be thus very useful for unambiguous location of the unsaturated system .

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REFERENCES and NOTES

1 . K. MORI, in The total synthesis of natural products, J. APSIMON Ed., vol. IV, p. 1-183, Wiley Interscience Publ. (1981) .

2 . G. JANSSEN and G. PARMENTIER, Biomed. Mass Spectrom., 5, 439 (1978) .

3 . M. BEROZA and B. A. BIERL, Anal. Chem., 39, 1131 (1967) .

4 . a) R. J. GREATHEAD and K. R. JENNINGS, Org. Mass Spectrom., 15, 431 (1980) and references therein ; b) E. BUSKER and H. BUDZIKIEWICZ, Org. Mass Spectrom., 14, 222 (1979) ; c) H. BUDZIKIEWICZ and E. BUSKER, Tetrahedron, 36, 255 (1980) ; d) J. H. TUMLINSON, R. R. HEATH and R. E. DOOLITTLE, Anal. Chem., 46, 1309 (1974) ; e) R. CHAI and A. G. HARRISON, Anal. Chem., 55, 969 (1983) ; f) J. C. TABET and J. EINHORN, Org. Mass Spectrom., in press .

5 . We recently heared from Dr J. H. TUMLINSON (U.S.D.A., Gainesville, Fl. U.S.A.) that results obtained from similar work in his laboratory will be published soon .

6 . CIMS was performed with a GC-MS NERMAG R10-10C equipment (France) with the following conditions : T (source) = 80°C, filament current = 200 μA, isobutane (99.95 %, Air Liquide, France) was used as reagent gas at a 0.3 Torr pressure giving a $C_4H_9^+/C_3H_7^+$ ratio = 3 . 50 ng-samples synthesized for most of them by already described methods (see ref. 1 and references therein) in the Laboratoire des Médiateurs Chimiques were introduced by GC : capillary column CPSil 5 (Chrompack, The Netherlands), 25 m, column temperature depending on the substrate .

7 . a) R. A. YOST and C. G. ENKE, Anal. Chem., 51, 1251 A (1979) b) P. H. DAWSON, J. B. FRENCH, J. A. BUCKLEY, D. J. DOUGLAS and D. SIMMONS, Org. Mass Spectrom., 17, 205 (1982) .

8 . The MS-MS spectra were obtained with a triple quadrupole MS/R-10-10 NERMAG at Ecole Normale Supérieure, Paris . Source conditions were the same than those indicated in ref. 6 . Laboratory energy was 35 eV and argon was used as collision gas in the second quadrupole . Samples were introduced *via* direct inlet probe .

9 . Unpublished results .

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